

CERTIFICATION

I, Samuel D. Larson, declare that I am well acquainted with the English and German languages and that, to the best of my knowledge, ability and belief, the attached translation of the German language application number 10/593,029 is a true and faithful translation of that document.

Date: _____

Signed: Samuel D. Larson

Our reference:

3294-018 DE-1

Direct dial: 0511/988 75 07

Date:

16 November 2004

Oxygen-bridged bimetallic complex, the production thereof, and its utilization for polymerization catalysis

The invention relates in general to the field of transition metal complex catalysts and metallocene catalysts for olefin polymerization.

Transition metal catalysts of the Ziegler-Natta type or catalysts systems developed therefrom have been widely used industrially for a long time as catalysts for low-pressure olefin polymerization, in particular the stereo selective polymerization of α -olefins. Chiral metallocene catalysts play an important role.

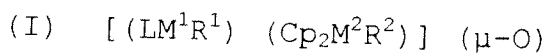
Cocatalysts used are organoaluminum compounds such as trialkylaluminum, alkylhaloaluminum, e.g. AlEtCl_2 or AlEt_2Cl , or, very widely, alkylaluminoxanes, in particular methylaluminoxane (MAO). To be able to achieve optimal catalytic activity for the respective system, a large excess of MAO cocatalyst is required. Thus, it is known that the catalytic activity of zirconocene-MAO systems decreases drastically below an Al:Zr ratio of about 200-300:1. It would therefore be desirable to have a catalyst which can be combined with smaller amounts of cocatalyst.

Because the mechanism of olefin polymerization catalyzed by transition metals is, like the structure of MAO, very complex and therefore not completely elucidated (Angew. Chem. 1995, 107, 1255-1283: "Stereospezifische Olefinpolymerisation mit chiralen Metallocencatalysatoren [Stereospecific Olefin Polymerization Using Chiral Metallocene Catalysts]", H-H. Brintinger, D. Fischer, R. M. Ihapt, B. Rieger, and R. Waymouth), the targeted design of

such complexes is difficult. A wide variety of catalyst systems have been tried with varying success. The production of stereochemically very uniform polymers having a narrow molecular weight distribution and also a good operating life of the catalysts used are frequently desired.

The object of the invention comprises discovering complexes having good catalytic activity in the polymerization of, in particular, olefins, which complexes avoid the disadvantages known in the prior art and have good operating lives and can be used particularly economically.

The subject matter of the invention is novel binuclear, oxygen-bridged, bimetallic complexes of the general formula (I) suitable for achieving this object:



where:

M^1 = Al, Ge, Zr or Ti;

M^2 = Zr, Ti, or Hf;

Cp = cyclopentadienyl;

R^1, R^2 = H; C(1-6) alkyl; halogen; aryl; $SiMe_3$ and alkylaryl with aryl = $C_6H_{5-n}X_n$, and X = halogen, C(1-6) alkyl, aryl, NO_2 , SO_3H , NR^3_2 , where R^3 = C(1-6) alkyl or H and n = 0 to 5; and L is a bidentate, doubly heteroatom-coordinated organic chemical ligand, which together with the metal M^1 forms a 5 or 6-membered ring. The heteroatom is preferably a nitrogen atom.

M^1 is preferably a main group metal, more preferably Al or Ge.

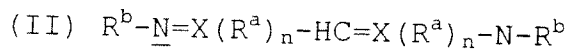
Primarily, chlorine, fluorine, and bromine come into consideration as the halogens and/or halides. In particular, mono, di, or trialkylphenyls are usable as the

alkylphenyls. C(1-6) alkyl stands for any branched or unbranched alkyl residue having from 1 to 6 carbon atoms, preferably methyl, ethyl, i-propyl, n-propyl or t-butyl. Aryl is a benzene residue bearing from 1 to 6 substituents and comprises phenyl. The aryl substituents can preferably be selected from the group consisting of halogen, C(1-6) alkyl, aryl, NO₂, SO₃H, NR³₂, where R³=C(1-6) alkyl or H. In addition to phenyl, another preferred residue is mesityl.

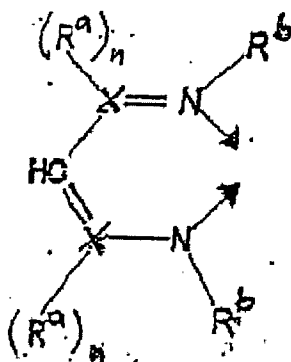
Surprisingly, it has been shown that the novel complexes are outstanding polymerization catalysts, as will be demonstrated hereafter with the aid of practical experimental data.

Preferred exemplary embodiments of the complexes according to the invention are heterobimetallic complexes, in particular oxygen-bridged aluminum-zirconocene complexes, preferably of the general formula [(LAlMe) (Cp₂ZrR²)] (μ-O), where R² is Me or Cl.

The ligand L preferably has the following composition according to formula II



corresponding to the structural formula:



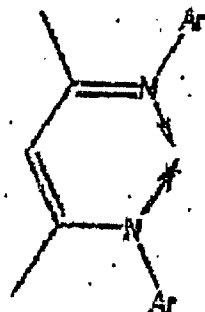
where: X = C or P;

R^a and R^b may be the same residues as specified for R^1 and R^2 , preferably H, methyl, ethyl, i-propyl, t-butyl, phenyl, alkylphenyl, trimethylsilyl;

$n = 1$ if $X = C$; $n = 2$ if $X = P$;

The ligand more preferably has the composition
 $Ar-\underline{N}=C(CH_3)-HC=C(CH_3)-\underline{N}-Ar$, where $Ar = 2,6-iPr_2C_6H_3$

corresponding to the structural formula:



where aryl is an aromatic system and is in particular 2,6- $iPr_2C_6H_3$.

To produce the oxygen-bridged bimetallic complexes according to the invention, we have found a method which is characterized in that a precursor complex of the formula $LM^1R^1(OH)$ is reacted with a metallocene precursor complex $Cp_2M^2(R^2)_2$ or $Cp_2M^2MeR^2$ or Cp_2M^2HX , where $X =$ halogen, preferably in an inert solvent. Primarily, fluorine, chlorine, or bromine comes into consideration as the halogen. Examples of the production method according to the invention are disclosed in the experimental part. These methods are particularly also suitable for producing heterobimetallic complexes in a targeted manner.

The invention also comprises the use of binuclear, oxygen-bridged bimetallic, in particular heterobimetallic, complexes which have been formed from a transition metallocene and an organic Al, Ge, Zr or Ti compound which

does not contain a cyclopentadienyl group, in particular a complex as claimed in any of claims 1 to 4, as polymerization catalysts. The complexes are particularly suitable for the homopolymerization or copolymerization of olefins, including α -olefins and cyclic olefins, for the cyclopolymerization of dienes and, if appropriate, for the polymerization of functionalized olefins. These catalysts are preferably used for the polymerization of low-pressure polyethylene.

A cocatalyst of the $[\text{MeAlO}]_x$ type, in particular methylaluminoxane (MAO), or else trialkylaluminum or an alkylhaloaluminum compound, is preferably used as the cocatalyst.

The invention therefore also comprises catalyst preparations for the polymerization of olefins, which preparations comprise at least one binuclear, oxygen-bridged, bimetallic complex according to the invention and at least one cocatalyst. Preference is given to using alkylaluminoxanes and in particular methylaluminoxane (MAO) as cocatalysts. Among the catalyst complexes according to the invention, preference is given to the heterobimetallic complexes.

As demonstrated by the experimental results, the catalyst complexes of the invention display very good catalytic activity. They reach a stable activity plateau within a short time and have good operating lives. It is surprising that the amount of cocatalyst (in the example MAO) required can be reduced by a multiple with the aid of the complex compounds according to the invention, in the example polymerizations carried out by up to 90%, compared to the Cp_2ZrMe_2 employed as reference.

Experimental part - examples

The preparation of exemplary compounds is described below, which were then studied for their catalytic activity in the polymerization of ethylene. The amount of cocatalyst was varied within a wide range.

A description of how LAlMe(OH) (2) can be obtained from the precursor compound LAlMeCl (1) by two different reaction routes will be given first.

The precursor compound (1) itself was synthesized as follows from commercially available starting materials:

Synthesis of LAlMe(Cl) (1): LLi-OEt_2 (2.49 g, 5.00 mmol) in toluene (30 ml) was added dropwise to MeAlCl_2 (5.00 ml, 1.0 M in hexane, 5.00 mmol) in toluene (15 ml) at -60°C . The mixture was warmed to room temperature and stirred for 12 hours. Volatile constituents were removed under vacuum and the crude product was dissolved in hexane (100 ml). The finished solution was concentrated to 50 ml and allowed to stand overnight at -32°C , in order to obtain colorless crystals. An additional amount of 1 could be recovered from the mother liquor. Yield: (2.05 g, 83%). Mp: 190°C , ^1HMR (500 MHz, C_6D_6): δ = 7.15-7.05 (m, Ar), 4.98 (s, 1 H, $\gamma\text{-CH}$), 3.76 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 2 H, CHMe_2), 3.21 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 2 H, CHMe_2), 1.52 (s, 6H, CMe), 1.46 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, CHMe_2), 1.28 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, CHMe_2), 1.19 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, CHMe_2), 1.02 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, CHMe_2), -0.65 (s, 3 H, AlMe); EI-MS: m/e (%); 479 (100) [$\text{M}^+ - \text{Me}$]; elemental analysis, calculated for $\text{C}_{30}\text{H}_{44}\text{AlClN}_2$ (494): C 72.9, H 8.9, N 5.6; found: C 72.8, H 9.0, N 5.6.

The LAlMe(OH) (2) is reacted with zirconocenes (bis(η -cyclopentadienyl) zirconium complexes) to form two different complexes, namely $[(\text{LAlMe})(\text{Cp}_2\text{ZrMe})] (\mu\text{-O})$ (3) and $[(\text{LAlMe})(\text{Cp}_2\text{ZrCl})] (\mu\text{-O})$ (4).

The associated reaction equations are shown in the figures.

In the figures:

- Figure 1: shows the preparation of LAlMeCl from LLiOEt_2 and MeAlCl_2 ;
- Figure 2a: shows the preparation of LAlMe(OH) from LAlMeCl using KH in a strongly basic medium;
- Figure 2b: shows the preparation of LAlMe(OH) from LAlMeCl using 1,3-di-*t*-butylimidazole,
- Figure 3: shows the preparation of $[(\text{LAlMe})(\text{Cp}_2\text{ZrMe})] (\mu\text{-O})$ from LAlMe(OH) and Cp_2ZrMe_2 .
- Figure 4: shows the preparation of $[(\text{LAlMe})(\text{Cp}_2\text{ZrCl})] (\mu\text{-O})$ from LAlMe(OH) and Cp_2ZrHCl .
- Figure 5: shows a plot of TOF values for catalyst 3 compared to the reference catalyst;
- Figure 6: shows a plot of reaction rates;
- Figure 7: shows the influence of the cocatalyst/catalyst ratio on the reaction rate.

General

All handling was carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. The samples for the recording of spectra and for reactions were processed in a glove box. The solvent was dried, distilled under nitrogen and degassed by customary methods before use.

The ^1H -NMR spectra were recorded on a Bruker AM 200 nuclear magnetic resonance spectrometer using SiMe_4 as external standard. The mass spectra were recorded on a Finnigan MAT 8230 mass spectrometer using the EI-MS method. The strongest peak of an isotope distribution is tabulated. The IR spectra were recorded in Nujol between KBr plates on a Bio-Rad FTS-7 spectrometer. The elemental analyses were carried out at the analytical laboratory of the Institute for Inorganic Chemistry of the University of Göttingen.

Synthesis of the precursor complex LAlMe(OH) (2): 40 ml of ammonia were condensed onto a suspension of LAlMeCl (1, 1.98 g, 4.00 mmol), KOH (KOH > 85%, H₂O 10-15%, 0.15 A, 2.33 mmol KOH (85%), 1.28 mmol H₂O (15%)), and KH (0.05 g, 1.25 mmol) in toluene (80 ml) at -78°C while stirring. The mixture was stirred at this temperature for a further one hour. The excess ammonia was then allowed to evaporate from the reaction mixture over a period of 4 hours. During this time, the mixture was slowly warmed to room temperature. After filtration and subsequent concentration under vacuum (to 8 ml), the resulting colorless solution was kept at -20°C for one week in order to isolate the colorless crystals of 2 (1.12 g). After separating off the crystals and subsequent partial removal of the solvent from the mother liquor, the colorless solution obtained was kept at -20°C for two days, and an additional yield of 2 (0.19 g) was recovered. Total yield: 1.31 g (68%, measured on 1). M.p.: 192°C; IR (Nujol) $\bar{\nu}$ = 3728, 1552, 1530, 1373, 1316, 1256, 1189, 1178, 1106, 1056, 1023, 940, 878, 805, 768, 757, 689, 614 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 7.16-7.07 (m, Ar), 4.93 (s, 1 H, γ -CH), 3.69 (sept, ³J_{HH} = 6.8 Hz, 2 H, CHMe₂), 3.25 (sept, ³J_{HH} = 6.8 Hz, 2 H, CHMe₂), 1.57 (s, 6 H, CMe), 1.32 (d, ³J_{HH} = 6.8 Hz, 12 H, CHMe₂), 1.21 (d, ³J_{HH} = 6.8 Hz, 6 H, CHMe₂), 1.07 (d, ³J_{HH} = 6.8 Hz, 6 H, CHMe₂), 0.53 (s, 1 H, OH); -0.88 (s, 3 H, AlMe) ; EI-MS: m/e (%) ; 461 (100) [M⁺ - Me]; elemental analysis: calculated for C₃₀H₄₅AlN₂O (476.7): C 75.6, H 9.5, N 5.9; found: C 75.4, H 9.5, N 6.0.

Alternative synthesis of 2 from 1: 1,3-di-tert-butyl-imidazol-2-ylidene (1.08 g, 6.00 mmol) in toluene (50 ml) were added to LAlMeCl (2.97 g, 6.00 mmol) in toluene (80 ml). The solution was stirred at room temperature for 10 minutes. Degassed and distilled water (108 μ l, 6.00 mmol) was slowly added over a period of 30 minutes while stirring. The mixture was stirred for a further one hour.

Volatile components were removed under vacuum and the crude product was extracted in hexane (150 ml), with the 1,3-di-tert-butylimidazolium chloride being filtered off through Celite. The solution finally obtained was concentrated (60 ml) and stored at -20°C for two days in order to give colorless crystals. Yield: 2.45 g (86%).

Synthesis of [(LAlMe) (Cp₂ZrMe)] (μ -O) (3): Toluene (60 ml) was added to a mixture of 2 (0.48 g, 1.00 mmol) and Cp₂ZrMe₂ (0.25 g, 1.00 mmol). The mixture was stirred at room temperature for 2 hours and then at 100°C for 24 hours. The resulting colorless solution was kept at room temperature for 48 hours in order to isolate colorless crystals of 3 (0.51 g). After concentrating the filtrate to 8 ml, the solution was kept at 0°C for three days. A further 0.15 g of 3 was obtained. Yield: 0.66 g (93%). M.p.: 385°C (dec); IR (Nujol) \square = 1518, 1467, 1380, 1316, 1257, 1178, 1101, 1017, 936, 884, 798, 768, 643, 617, 449 cm^{-1} ; ^1H NMR (300 MHz, CDCl₃): δ = 7.25-7.24 (m, Ar), 5.31 (s, 10 H, Cp), 5.06 (s, 1 H, γ -CH), 3.17 (sept, $^3J_{\text{HH}}$ = 6.8 Hz, 2 H, CHMe₂), 3.15 (sept, $^3J_{\text{HH}}$ = 6.8 Hz, 2H, CHMe₂), 1.75 (s, 6 H, CMe), 1.37 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 6 H, CHMe₂), 1.35 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 6H, CHMe₂), 1.22 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 6 H, CHMe₂), 1.03 (d, J_{HH} = 6.8 Hz, 6 H, CHMe₂), -0.32 (s, 3 H, ZrMe), -0.72 (s, 3 H, AlMe); EI-MS: m/e (%): 695 (100) [M^+ -Me]; elemental analysis: calculated for C₄₁H₅₇AlN₂OZr (712.1): C 69.2, H 8.1, N 3.9; found: C 69.3, H 7.9, N 3.9.

Synthesis of [(LAlMe) (Cp₂ZrCl)] (μ -O) (4): In a similar method to that used for the preparation of 3, toluene (60 ml) was added to a mixture of 2 (0.48 g, 1.00 mmol) and Cp₂ZrHCl (0.25 g, 1.00 mmol). The colorless solution obtained was kept at room temperature for 48 hours in order to isolate colorless crystals of 4 (0.37 g). After concentrating the filtrate to 10 ml, the solution was kept at 0°C for three days. A further 0.28 g of 4 was obtained. Yield: 0.65 g (89%). M.p. : 396°C (dec); IR (Nujol) \square

=1530, 1466, 1380, 1315, 1254, 1181, 1098, 1022, 943, 860, 797, 778, 759, 725, 657, 617 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ = 7.29-7.21 (m, Ar), 5.54 (a, 10 H, Cp), 5.09 (s, 1 H, γ -CH), 3.16 (sept, $^3J_{\text{HH}}$ = 6.8 Hz, 2 H, CHMe_2), 3.15 (sept, $^3J_{\text{HH}}$ = 6.8 Hz, 2H, CHMe_2), 1.78 (s, 6 H, CMe), 1.42 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 6 H, CHMe_2), 1.36 (d, $^3J_{\text{HH}}$ = 6.8, 6 H, CHMe_2), 1.24 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 6 H, CHMe_2), 1.02 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 6 H, CHMe_2), -0.66 (s, 3 H, AlMe); EI-MS: m/e (%): 715 (100) [M^+ - Me]; elemental analysis: calculated for $\text{C}_{40}\text{H}_{54}\text{AlClN}_2\text{OZr}$ (732.5): C 65.6, H 7.4, N 3.8; found: C 65.5, H 7.3, N 3.9.

Polymerization of Ethylene

Catalyst (0.005 M in toluene, 4 ml, 20 μmol) was added to toluene (100 ml) in a 250 ml Schlenk flask. This solution was degassed and the system was then connected to an ethylene atmosphere (1013 mbar pressure). The associated aluminoxane (toluene solution) was added. After the mixture obtained had been stirred for an appropriate time, the reaction was stopped by means of ethanol and the white polyethylene (PE) was collected and dried. The results are shown in Table 1 and Figure 5.

Determination of the TOF Value and the Polymerization Rate

g grams of polyethylene were obtained in 0.5 hours. The TOF value was then calculated according to:

$$\text{TOF} = \frac{\text{g PE}}{20 \times 10^{-6} (\text{mole cat}) \times 0.5 (\text{h})} = \frac{\text{g}}{10} \times 10^6 (\text{g PE/mole cat h})$$

When the ethylene volume V (consumed when the pressure of the system has dropped to 27 mbar below atmospheric pressure) has been polymerized in t seconds (when t is less than 1 sec, it is difficult to determine the reaction time

precisely), the reaction rate is $r=V/t$ (Table 2 and Figure 6).

Influence of the Concentration of 3 on the TOF value

Explanations of the data in Table 1: using the method as described above, 3 (0.005 M in toluene, 3 ml, 15 μ mol), for example, was added to toluene (100 ml). MAO (0.15 ml) was added while stirring. After 20 minutes, MAO (1.5 ml) was added and the polymerization was started. After the resulting mixture had been stirred for 30 minutes, PE (9.9 g) was obtained (experiment number A08). Using the same method, MAO (0.1 ml) was added to a solution of 3 (2 ml, 10 μ mol). After 20 minutes, MAO (1.0 ml) was added again. After polymerization for 2 hours, PE (7.6 g) was obtained (experiment number A09). The results and conditions for various experiments are summarized in Table 1. The experiments denoted by A and B relate to the catalysts according to the invention, and the experiments denoted by D relate to reference experiments.

Influence of the Reaction time of 3 with MAO on the TOF value

Using the same method, 1.7 ml or 3.4 ml of MAO were added to 3 (20 μ mol). After 18 or 30 minutes, 6.2 g or 10.9 g, respectively, of PE were obtained (experiment numbers A10 and A11 in Table 1).

The tabular data for 3 and the reference example are shown graphically in Figure 5. It can be seen that the novel catalyst achieves a high level of the TOF value even at very much smaller amounts of cocatalyst.

In Figure 6, the reaction rate is plotted against the reaction time for 5 catalyst mixtures (A) with MAO and, for comparison, three Cp_2ZrMe_2 (D) systems with MAO. It can be

seen that the novel catalyst mixtures (A07-A03) show constant behavior as a function of time, while this is not the case for the known (Cp_2ZrMe_2) mixtures.

In Figure 7, the reaction rate is plotted as a function of the reaction time. Once for the novel catalyst system and MAO (A02) in a ratio of MAO to catalyst of 48:1 and, for comparison, Cp_2ZrMe_2 in a ratio of MAO to catalyst of 176:1 (D05). It can clearly be seen that the novel system A02 still has approximately twice the reaction rate after 60 minutes. It has to be noted that only approximately one-fourth of the amount of MAO was used in the novel A02 system.

Table 1: TOF (g PE/mol cat·h x 10⁻⁶) values for catalysts 3, 4 and Cp₂ZrMe₂

Catalyst*	MAO: cat	t (min)	PE (g)	TOF
3 (A01)	32	60	0.89	0.05
3 (A02)	48	60	7.8	0.39
3 (A03)	96	30	9.0	0.90
3 (A04)	136	30	10.9	1.09
3 (A05)	176	30	11.9	1.19
3 (A06)	272	30	12.4	1.24
3 (A07)	400	30	12.7	1.27
3 (A08)	176	30	9.9	1.32
3 (A09)	176	120	7.6	0.39
3 (A10)	136	18	6.2	1.03
3 (A11)	272	30	10.9	1.09
4 (B04)	136	30	8.4	0.84
4 (B05)	176	30	11.4	1.14
Cp ₂ ZrMe ₂ (D04)	136	120	3.3	0.08
Cp ₂ ZrMe ₂ (D05)	176	73	12.8	0.52
Cp ₂ ZrMe ₂ (D06)	272	60	14.6	0.73
Cp ₂ ZrMe ₂ (D07)	400	37	14.8	1.20

* For experiments A01 to A07, 0.2 ml of MAO was added to a solution containing 3. After 20 minutes, the remaining MAO was added and the polymerization was started.

Table 2: Polymerization reaction rates r (V/seconds) for the catalysts 3 and Cp_2ZrMe_2

A03		A04		A05		A06		A07		D05		D06		D07	
t	r	t	r	t	r	t	r	t	r	t	r	t	r	t	r
0.96	0.03	1.33	0.04	0.85	0.08	0.68	0.07	0.20	0.08	2.10	0.043	0.98	0.13	1.97	0.20
2.52	0.05	2.92	0.07	1.98	0.13	1.62	0.13	1.10	0.20	4.00	0.045	3.23	0.14	4.50	0.25
4.21	0.08	4.23	0.11	2.42	0.16	2.60	0.25	1.40	0.25	6.85	0.053	5.25	0.17	6.80	0.33
5.72	0.13	5.96	0.20	3.30	0.25	3.18	0.33	1.75	0.33	10.50	0.067	6.83	0.20	8.70	0.50
6.98	0.20	6.69	0.25	3.90	0.33	3.52	0.42	2.03	0.40	15.85	0.091	8.23	0.25	10.92	1.00
7.67	0.25	7.68	0.33	4.30	0.40	4.30	0.67	2.27	0.50	21.48	0.125	10.63	0.33	12.18	1.00
8.98	0.33	8.95	0.50	5.75	0.80	4.83	0.92	2.72	0.67	24.90	0.143	13.00	0.50	14.80	0.50
11.37	0.50	9.80	0.77	6.60	1.00	5.35	1.00	3.58	1.00	28.00	0.167	17.93	1.00	19.33	0.40
13.92	0.67	10.38	1.00	10.70	1.00	9.56	1.00	8.25	1.00	30.88	0.200	22.88	0.50	30.00	0.33
15.58	0.72	12.97	1.00	12.80	0.67	11.25	0.78	11.50	0.07			25.78	0.33		
17.48	0.67	16.37	0.67	16.58	0.50	12.58	0.67	16.30	0.50			30.00	0.29		
21.00	0.50	20.77	0.40	19.30	0.44	15.30	0.54	17.91	0.46						
24.20	0.40	24.12	0.37	22.01	0.40	23.81	0.38	21.20	0.40						
29.48	0.33	30.00	0.33	29.59	0.37	29.95	0.35	30.00	0.35						

ML/dk